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(54) Title: CHROME-FREE SIZING FOR GLASS FIBER GUN ROVING (57) Abstract Chrome-free aqueous sizing composition for glass fiber gun roving contains a mixture of emulsified film-forming polymers, titanium acetyl acetate, silylated polyazamide, cationic lubricant and methacryloxy-propylsilane.		

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D E S C R I P T I O N

10. CHROME-FREE SIZING FOR GLASS FIBER GUN ROVING

TECHNICAL FIELD

This invention relates to the field of sizing compositions for glass fibers, and more particularly, for
15 glass fiber gun roving, and to glass fibers coated therewith.

BACKGROUND ART

Glass fibers used as reinforcing elements in polymeric or resinous matrix materials are usually coated
20 with a very light-weight size coating which serves to protect the fibers from damage by abrasion during processing, handling and/or use, to bind the individual fibers into more-or-less tightly integrated multi-fiber bundles or strands, and/or to enhance the reinforcing
25 interaction between the fibers and the resinous matrix in which they are imbedded as reinforcing elements. Such sizing compositions are frequently applied to the glass fibers at the time of their initial production, which is ordinarily by pulling a plurality of streams of molten
30 glass issuing from a reservoir thereof through a substantially corresponding plurality of suitable orifices so as to attenuate these streams to the desired fiber diameter as they cool and solidify. The sizing composition is typically applied to the individual fibers in-line as
35 soon as they have cooled sufficiently below the solidification temperature, which cooling may be accelerated by wetting the newly solidified but still hot



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1 fibers with water. Liquid sizing compositions are applied
in such situations by spraying, by drawing the fibers
across a suitable roll, belt, apron, pad, etc. wet with the
liquid sizing composition, or other conventional liquid
5 coating methods. After the liquid sizing composition has
been applied to the individual advancing glass fibers, they
are typically brought together while still at least
partially wet with the liquid sizing composition into one
or more multifiber bundles or strands, which may be
10 collected into a suitable package for further processing,
storage and/or shipment, as by winding onto a rotating
collet. The wet fibers or strands are normally dried,
before and/or after such collection, to deposit the
non-volatile residue of the liquid sizing composition onto
15 the surfaces of the fibers.

Liquid sizing compositions suitable for such
application to glass fibers ordinarily are dilute
solutions, dispersions and/or emulsions, often in aqueous
media, of a film-forming polymer or resin, a lubricant and
20 a coupling agent. Other components, such as anti-static
agents (especially where the sized glass fibers are to be
chopped into short lengths while dry), emulsifying or
solubilizing agents, viscosity modifying agents, etc. have
also sometimes been incorporated in such liquid sizing
25 compositions.

One of the uses for glass fibers is as gun
roving, which desirably consists of a plurality of
continuous strands weakly integrated together, with each
strand consisting of a plurality of individual glass fibers
30 tightly integrated together by the size coating on the
fibers. Such gun roving is used by feeding it through a
suitable chopper incorporated in or closely associated with
a suitable gun for spraying a fluid resin composition
together with the chopped roving onto a mold or other
35 suitable target so that the chopped roving or pieces of
strand separated therefrom becomes imbedded in the fluid
resin, which will subsequently be solidified by cooling



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1 and/or by curing by chemical reaction. Representative
equipment and corresponding methods for such use of glass
fibers in gun roving are described in U.S. Patent No.
3,111,440, entitled DEVICES AND METHODS FOR APPLYING
5 STRANDS, issued November 19, 1963 for an invention of
William H. Prentice. Typically, the chopped pieces are
from about 1.27 cm to about 5.08 cm (1/2 to about 2 inches)
in length.

Glass fiber gun roving has heretofore been coated
10 with liquid sizing compositions containing Werner-type
chrome complexes, such as methacrylate chromic chloride,
which is thought to function in part at least as a
glass-resin coupling agent, although such chrome complexes
have sometimes been used together with conventional
15 organosilane glass-resin coupling agents. Before the
present invention it had not been thought possible to
achieve a satisfactory balance of desirable properties in
glass fiber gun roving without the inclusion of a chrome
complex in the sizing composition for the constituent
20 fibers thereof, and particularly to achieve a desirable
ease and completeness of chopping in conventional
equipment, while also achieving desirably rapid and
complete wetting of the chopped reinforcement by the liquid
matrix resin composition and providing a desirable
25 enhancement of the physical properties of the resinous
matrix while holding the generation of fuzz, from breakage
of fibers during processing of the continuous strand or
roving, and "fly", i.e., static-dispersed pieces of chopped
roving strand or partially or fully fibrillated residues
30 thereof accompanying the chopping and spraying at the gun,
to desirably low incidence.

DISCLOSURE OF INVENTION

A substantially chrome-free aqueous sizing
composition for glass fiber gun roving which comprises (A)
35 a mixture of emulsified film-forming polymers comprising a
polymer of vinyl acetate and ethylene, a polymer of vinyl
acetate and an epoxy-functional vinyl monomer, and an



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- 1 unsaturated polyester resin; (B) titanium acetyl acetonate;
(C) a silylated polyaminopolyamide hydrochloride or
hydrolysate thereof; (D) a cationic lubricant; and (E)
3-methacryloxypropyltrimethoxysilane or hydrolysate
5 thereof.

BEST MODE OF CARRYING OUT INVENTION

- The emulsified film-forming polymer components of the present invention can be any emulsified polymers of the types called for which will coalesce to form coherent
10 films, and which preferably will so coalesce at normal ambient workplace temperatures. A small amount of suitable plasticizer to aid in such coalescence, of which many are known and available, may be blended and co-emulsified with one or more of the polymers, if desired, but it is
15 ordinarily found possible and preferable to select polymers which do not require such additives to exhibit advantageous characteristics in use. However, it is nonetheless desirable and preferred to include a latently reactive unsaturated plasticizer with the unsaturated polyester
20 resin to ultimately react with this unsaturated polyester and with an unsaturated polyester matrix resin to more intimately bond the glass fibers to each other and to the matrix in which they are imbedded as reinforcing elements.

- A particularly suitable emulsified polymer of
25 vinyl acetate and ethylene is available as Airflex 410 (TM/Air Products and Chemicals Co.), an aqueous emulsion containing about 55% by weight non-volatiles comprising a vinyl acetate-ethylene copolymer having a glass transition temperature of about 2°C. non-ionically emulsified as
30 particles of about 0.4 μ m average diameter.

- A particularly suitable emulsified polymer of vinyl acetate and an epoxy-functional vinyl monomer is available as Resyn 25-1971 (TM/National Starch and Chemical Corp.), an aqueous emulsion containing about 54.5 \pm 1% by
35 weight non-volatiles comprising a copolymer of vinyl acetate with about 2% by weight of glycidyl methacrylate non-ionically emulsified.

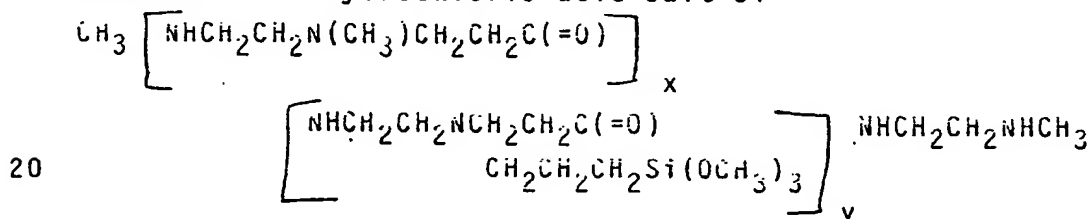


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1 A particularly suitable unsaturated polyester
resin is available as MR70D (TM/United States Steel Corp.),
an approximately 60:40 by weight blend of an unsaturated
polyester and diallyl phthalate, a latently reactive
5 plasticizer, which was non-ionically emulsified to form an
aqueous emulsion containing about 59% by weight
non-volatiles and designated PE-700.

A particularly suitable titanium acetylacetonate
is available as Tyzor AA (TM/E.I. duPont de Nemours, Inc.),
10 a 75% by weight solution or dispersion of bis(2,
4-pentanedionate-U,U')bis(2-propanolato) titanium in
isopropanol.

A particularly suitable silylated polyamino
polyamide hydrochloride is available as Y-9567 (TM/Union
15 Carbide Corp.), an 80% by weight dispersion or solution in
methanol of a hydrochloric acid salt of



where $x + y$ is a number from about 3 to about 10. Such
materials and their preparation are described in detail in
U.S. Patent No. 3,746,738, entitled SILICON CONTAINING
25 POLYAZIMIDES issued July 17, 1973 for an invention of
Enrico J. Pepe and James G. Marsden.

A particularly suitable cationic lubricant is a
weak acid salt of a partial fatty amide of a polyamine such
as Emery 6760 U (TM/Emery Industries, inc.), a 65% by
30 weight aqueous solution or dispersion of an acetic acid
salt of a partial amide of mixed fatty acids having about 6
to 8 carbon atoms with a polyethylenamine. The same
material has also been available undiluted as Emery 6717.

A particularly suitable
35 γ -methacryloxypropyltrimethoxysilane is available in a
blend with a proprietary stabilizer as A-174 (TM/Union
Carbide Corp.) The silane is preferably hydrolyzed in



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1 dilute aqueous weak acid before use.

While the proportions of the various components of the aqueous sizing compositions of the invention are not narrowly critical, it is preferred that they be within
5 about the following ranges:

	<u>Component</u>	<u>Preferred Weight %</u>
	Emulsified polymer of vinyl acetate and ethylene	1-5
10.	Emulsified polymer of vinyl acetate and an epoxy-functional vinyl monomer	1-5
	Emulsified unsaturated polyester resin	0.5-1.5
15	Titanium acetyl acetate	0.5-1.5
	Silylated polyaminopolyamide hydrochloride	0.01-0.2
	Cationic lubricant	0.005-0.1
	3-methacryloxypropyltrimethoxy	0.005-0.1
20	silane	

Other components can be included, if desired, but in order to ensure that the advantages of the invention are realized, it is preferred that other components be omitted unless it is found that no significant diminution of those
25 advantages results from the inclusion thereof. In particular, since it is a principal object of the invention to provide a chrome-free sizing composition for glass fiber gun roving, no chromium compounds or complexes should be included in sizing compositions of the invention. However,
30 since some of the components, e.g. the titanium acetyl acetate, the silylated polyaminopolyamide, and the cationic lubricant, are solubilized by acids and/or lower alcohols, the inclusion of minor additional amounts of alcohols such as methanol, ethanol, propanol, isopropanol,
35 etc. and/or acids such as hydrochloric or acetic may be found desirable.

The aqueous sizing compositions of the invention



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1 can be prepared following generally accepted mixing
practices. These sizing compositions can be applied to the
glass fibers using any convenient method. The amount of
aqueous sizing composition applied is not narrowly
5 critical, but is preferably controlled so as to deposit on
the glass fibers a size coating comprising the in situ
dried residue of the aqueous sizing composition of the
invention in an amount from about 0.5 to about 2 percent of
the weight of the glass, taking into account the dilution
10 of the non-volatile components in the aqueous sizing
composition and the usual mechanical loss of some of the
aqueous composition initially applied to the fibers before
it is dried thereon.

Preferably, the aqueous sizing composition is
15 applied to the glass fibers as they are produced by
continuous drawing from the melt. While the aqueous sizing
composition on the fibers may be at least partially dried
before collection into a package, it is entirely
satisfactory to gather the wet fibers into strands,
20 preferably with about 100 to about 300 and more preferably
about 200 individual fibers to each strand, collecting
these strands into packages as by winding on a collet,
which also provides the tension for drawing the fibers, and
then heating the package in a conventional circulating hot
25 air oven to drive off volatile materials and deposit the
non-volatile components of the sizing composition as a size
coating on the fibers which will also bind together the
individual fibers into a tightly integrated strand.

The integrated continuous glass fiber strands can
30 be roved together in weakly integrated roving, preferably
of about 30 to about 70 strands each, to produce a
continuous glass fiber gun roving. While the diameter of
the individual glass fibers is not narrowly critical,
diameters from about $10\mu\text{m}$ to about $13\mu\text{m}$ are preferred.

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EXAMPLE 1

Particularly advantageous chrome-free aqueous
sizing compositions for glass fiber gun roving,



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1 representative of the present invention, were prepared according to the following formulations:

	Component	Weight %			
		A		B	
		As rec'd.	Active	As rec'd.	Active
5	Airflex 410 (55%)	5.10	2.80	5.10	2.80
	Resyn 25-1971 (54.5%)	4.45	2.45	4.45	2.45
	PE-700 (59%)	1.25	0.74	1.25	0.74
	Tyzor AA (75%)	1.10	0.82	1.10	0.82
10	Y-9567 (80%)	0.03	0.024	0.10	0.08
	Emery 67600 (65%)	0.03	0.02	0.03	0.02
	A-174	0.015	0.015	0.015	0.015
	Isopropanol	2.00	--	2.00	--
	Acetic acid	0.005	0.005	0.005	0.005
15	D.I. water	Balance		Balance	

Both A and B formulations had non-volatile content of about 0.0+0.5 percent by weight and pH of about 3.6 to 4.9.

These compositions were applied to both H-fibers (about 10.1 to about 11.4 μ m in diameter) and J-fibers (about 11.4 to about 12.7 μ m diameter) with a conventional applicator as they were drawn from the melt, the wet fibers gathered into strands of about 200 individual fibers and wound into packages on a rotating collet in groups of 4 strands. The packages were dried in a conventional circulating hot air oven maintained at about 150°C (265° F) for about 12-14 hours, depending on the size of the package. The dried size coating thus deposited on the glass fibers constituted about 1.0 to about 1.3 percent of the weight of the glass and tightly integrated the strands. The strands from 13 packages of each type of H-fibers and 11 packages of each type of J-fibers were roved separately into weakly integrated gun roving by conventional means.

The glass fiber gun rovings so produced were found to exhibit exceptionally advantageous combinations of properties, particularly in view of the sizing compositions being chrome-free. Thus, they were found to chop easily and cleanly, to produce advantageously low levels of fuzz



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1 and fly, to wet out rapidly and fully with conventional
unsaturated polyester matrix resins (the H-fiber roving
being especially useful with unfilled matrix resin systems
and the J-fiber roving with more viscous filled matrix
5 resin systems, both of which can be chemically thickened,
if desired). The dried strands unwound freely from the
packages during roving with little or no disintegration of
the strands, and the strands were sufficiently integrated
in the roving so that post-cure of the size coating after
10 roving was not required, but upon chopping and spraying at
the gun, the pieces of roving separated advantageously into
pieces of strand, which maintained good integrity.

The unsaturated polyester resin laminates formed
with these rovings exhibited excellent tensile strength and
15 modulus, flexural strength and modulus both dry and after
immersion in boiling water for 24 hours, impact strength,
and other desirable characteristics.

Numerous variations and modifications of the
invention as particularly described herein will be apparent
20 to those skilled in the art, and such variations and
modifications are intended to be comprehended within the
scope of the invention.

INDUSTRIAL APPLICABILITY

The invention described herein is readily
25 applicable to the glass fiber industry.

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C L A I M S

1. A substantially chrome-free aqueous sizing
10 composition for glass fiber gun roving which comprises (A)
a mixture of emulsified film-forming polymers comprising a
polymer of vinyl acetate and ethylene, a polymer of vinyl
acetate and an epoxy-functional vinyl monomer, and an
unsaturated polyester resin; (b) titanium acetyl acetate;
15 (C) a silylated polyamino-polyamide hydrochloride or
hydrolysate thereof; (D) a cationic lubricant; and (E)
3-methacryloxypropyltrimethoxysilane or hydrolysate
thereof.

2. An aqueous composition according to claim 1
20 wherein the proportions by weight of the components
relative to the total weight of the aqueous composition,
are about:

(A) 1 to 5% of said emulsified polymer of
vinylacetate and ethylene, 1 to 5% of said emulsified
25 epoxy-functional vinyl monomer, and 0.5 to 1.5% of said
emulsified polyester resin;

(B) 0.5 to 1.5% of said titanium acetyl
acetate;

(C) 0.01 to 0.2% of said silylated polyamide
30 hydrochloride;

(D) 0.005 to 0.1% of said cationic lubricant;
and

(E) 0.005 to 0.1% of said silane.

3. An aqueous composition according to claim 2
35 wherein said epoxy-functional vinyl monomer is glycidyl
acrylate or methacrylate, said unsaturated polyester resin
comprises a minor proportion by weight at an unsaturated



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1 plasticizer latently reactive therewith, and said cationic
lubricant is a weak acid salt of a partial fatty acid amide
of a polyamine.

4. A glass fiber coated with the in situ dried
5 residue of an aqueous composition according to claim 1.

5. A glass fiber coated with the in situ dried
residue of an aqueous composition according to claim 2.

6. A glass fiber coated with the in situ dried
residue of an aqueous composition according to claim 3.

10. 7. A coated glass fiber according to claim 4
wherein the coating comprises about 0.5 to about 2 percent
of the weight of the glass.

8. A glass fiber according to claim 5 wherein
the coating comprises about 0.5 to about 2 percent of the
15 weight of the fiber.

9. A glass fiber according to claim 6 wherein
the coating comprises about 0.5 to about 2 percent of the
weight of the fiber.

10. A glass fiber gun roving comprising a
20 plurality of coated glass fibers according to claim 4.

11. A glass fiber gun roving comprising a
plurality of coated glass fibers according to claim 5.

12. A glass fiber gun roving comprising a
plurality of coated glass fibers according to claim 6.

25 13. A glass fiber gun roving according to claim
12 wherein the fibers are about 10 to about 13 μ m in
diameter.

14. A glass fiber roving according to claim 13
comprising about 30 to about 70 strands weakly integrated
30 with each other, each strand comprising about 100 to about
300 of said coated glass fibers tightly integrated into
said strand by the coating on said fibers.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US84/01525

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ³ C08K 3/40; US// 428/378, 428/388, 428/389, 428/391, 428/394; 523/200, 206, 217, 501, 503, 509		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
US	428/378 428/391 523/200 523/501 524/254 428/388 428/394 523/206 523/503 524/284 428/389 523/217 523/504	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 3,754,971 PUBLISHED 28 AUGUST 1973 PEPE ET AL	1-14
A	US, A, 3,802,953 PUBLISHED 9 APRIL 1974 MARZOCCHI	1-14
A	US, A, 3,933,711 PUBLISHED 20 JANUARY 1976 MOTSINGER ET AL	1-14
A	US, A, 3,968,068 PUBLISHED 6 JULY 1976 HAGGERTY	1-14
A	US, A, 4,126,729 PUBLISHED 21 NOVEMBER 1978 RICHARDSON	1-14
A	US, A, 4,178,412 PUBLISHED 11 DECEMBER 1979 SAGE ET AL	1-14
A	US, A, 4,233,809 PUBLISHED 18 NOVEMBER 1980 GRAHAM	1-14
A	US, A, 4,244,844 PUBLISHED 13 JANUARY 1981 MOLINIER ET AL	1-14
<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report *	
22 OCTOBER 1984	13 NOV 1984	
International Searching Authority *	Signature of Authorized Officer ²⁰	
ISA/US	HERBERT J. LIDLING	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 4,291,136 PUBLISHED 12 SEPTEMBER 1981 KEOGH	1-19
A	US, A, 4,338,233 PUBLISHED 6 JULY 1982 DAS ET AL	1-14
A	US, A, 4,341,877 PUBLISHED 21 JULY 1982 DAS ET AL	1-14

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the international searching authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.